Registry No. CO, 630-08-0; HI, 10034-85-2; CH_3CO_2H, 64-19-7; $CH_3CH_2CO_2H$, 79-09-4.

Supplementary Material Available: References (2 pages). Ordering information is given on any current masthead page.

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Transition Metal/Acid Induced Reductive Coupling of Carbon Monoxide

Summary: Carbon monoxide is converted to acetic acid and to glycolic acid by solutions containing acid and compounds of palladium, rhodium, platinum, and iridium; glycolic and acetic acids are produced in the presence of HCl or H_3PO_4 but, in the presence of iodide, acetic acid alone is produced.

Sir: We report reductive coupling of carbon monoxide to acetic acid and to glycolic acid.

The conversions were effected by solutions containing acid, either introduced as such or formed in situ, and compounds of transition metals.[1-3]

$$\mathrm{CO} + \mathrm{H_2} \xrightarrow[\text{acid}]{\text{compound of Pd, Rh, Pt, or Ir}} \mathrm{CH_3CO_2H,\ HOCH_2CO_2H}$$

Acetic acid has been produced from CO and H_2 by reaction on supported heterogeneous transition-metal catalysts and by reaction with solutions containing ruthenium[4a]; we have recently described its formation from CO and aqueous HI in the absence of a metal.[4b]

Representative results obtained by use of compounds of palladium in the presence of acids containing halide or phosphate are in Tables I and II.[5] Glycolic acid was produced by palladium in combination with HCl or H_3PO_4 (Table I); both palladium and acid are necessary (Table I, note *b*). In the presence of iodide, acetic acid alone was produced by reaction of CO or CO/H_2 (Table II). Palladium is used in an amount greater than the molal amounts of products.

On the basis of reports in the literature and our own observations, we believe that a body of indirect evidence exists that is consistent with a pathway resembling CO → ($HC(=O)CO_2H$, CH_2O) → $HOCH_2CO_2H$ → CH_3CO_2H for the formation of products: (1) See ref 4b for a discussion of the transformations $CO + H_2O \rightarrow HCO_2H$; $2CO + H_2O \rightarrow HO_2CCHO$; $CO + HX \rightarrow HCOX$; $HCO_2H + CO + H_2O \rightarrow HO_2CCHO$; $HCOI + HI \rightarrow CH_2O + I_2$; $HO_2CCHO \rightarrow CH_2O$; $HO_2CCHO \rightarrow HOCH_2CO_2H$; $CH_2O + CO + H_2O \rightarrow CH_3CO_2H, HOCH_2CO_2H$; $HO_2CCHO \rightarrow HO_2CCH_2OH$; $HOCH_2CO_2H \rightarrow CH_3CO_2H$ in the absence of a metal. (2) The palladium-catalyzed reduction of acyl halides is well-known. (3) The acid-catalyzed conversion of a glycoloyl–metal compound to an acetyl compound, $ROCH_2C(=O) \rightarrow CH_3C(=O)$, is known.[6] (4) It was reported that trioxane (formaldehyde trimer), water, and HI reacted with 1000 psi of CO at 150 °C in the presence of $PdCl_2$ to give $HOCH_2CO_2H$, CH_3CO_2H, and HCO_2H;[7] we made similar observations upon addition of formaldehyde (20 mmol) to the $PdCl_2$/water system of Table I. (5) In contrast, addition of CH_3OH (21, 18, and 11 mmol) to the $PdCl_2$ system in water, 30% aqueous HCl, and 65% aqueous HI, respectively, resulted in the formation of products in amounts very similar to those given in Tables I and II, respectively.[8,9] (6) Addition of $HOCH_2CO_2H$ (18 mmol) to the $PdCl_2$/30% aqueous HCl and $PdCl_2$/water systems gave a yield of CH_3CO_2H that was 55% and 18%, respectively, after exclusion of any amount produced (Table I) in the absence of added $HOCH_2CO_2H$. (7) The $CH_3CO_2H/HOCH_2CO_2H$ ratio increased and the amount of $HOCH_2CO_2H$ decreased with increases in time and in [HCl] (Table I). (8) In the presence of I^-, anticipated to be better than Cl^- at effecting a metal/acid catalyzed conversion of ROH to RH, only CH_3CO_2H was observed (Table II vs. Table I).

Other metals also effected these reactions: (a) $Rh(CO)_2acac$ (1.5 mmol), in sulfolane[10] at 250 °C and 12500 psi of 1/1 CO/H_2, combined with HI (3 mmol), I_2 (1.5 mmol), or ZnI_2 (150 mmoles)[11] gave 2–5 g of CH_3CO_2H in 4 h. (b) Under conditions similar to those used for palladium (Table I), $Ir_4(CO)_{12}$ (1.2 mmol) in 30% aqueous HCl and $IrCl_3$ (10 mmol) in water each produced ~0.05 g of CH_3CO_2H; Ir powder produced none. Under 5000 psi of CO and otherwise similar (Table I) conditions, Na_3IrCl_6 (4 mmol) in 30% aqueous HCl and in water produced 0.08 and 0.03 g, respectively, of CH_3CO_2H. (c) Under conditions similar to those used for palladium (Table I), $PtCl_2$ (10

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(1) A unified discussion of "acid catalysis" and "transition metal catalysis" is provided as Supplementary Material.

(2) For a review of proton-induced reduction of CO, see Shriver, D. F. in "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 152, p 1.

(3) References to the use of compounds of Pd, Ir, Pt, Ru, and Rh in the presence of acid as ionic hydrogenation catalysts, e.g., as "hydride-transfer agents" to electrophilic centers, are provided as Supplementary Material.

(4) (a) J. F. Knifton has reported the $RuO_2/[Mn_2(CO)_{10}$, $Mn(acac)_3$, $MnCO_3$, or $Re_2(CO)_{10}]$-, [RuO_2, $Ru(acac)_3$, or $Ru_3(CO)_{12}]/[Co(acac)_3$ or $Co_2(CO)_8]$-, and [RuO_2 or $Ru(acac)_3]/[Ti(acac)_2(OBu)_2$, $Ti(OMe)_4$, or $Ti(acac)_3]$-catalyzed conversion of CO/H_2 to acetate esters in molten R_4PX at 4000–6000 psi and 220 °C in U.S. Patents 4332914, 4332915, and 4339545, 1982, respectively. G. Jenner, A. Kiennemann, E. Bagherzadah, and A. Deluzarche (*React. Kinet. Catal. Lett.* **1980**, *15*, 103) reported the $RuCl_3 \cdot 3H_2O$- and RuO_2-catalyzed conversion of 1-propanol to *n*-propyl acetate by 1100 atm of 1/1 CO/H_2. D. W. Smith (British Patent Publication 2074164A, 1981) reported the formation of CH_3CO_2H and $CH_3CO_2CH_3$ in unreported amounts as products of the reaction of CO/H_2 with halogen-containing ruthenium catalysts in *N-methyl*pyrrolidone as solvent at ~500 atm. (b) Kaplan, L., preceding communication in this issue.

(5) A discussion of the chemistry of palladium in the presence of CO, anions, and/or acids and of the chemistry of palladium carbonyl halide anions is provided as Supplementary Material.

(6) For example, see Cutler, A.; Bodnar, T.; Coman, G.; LaCroce, S.; Lambert, C.; Menard, K. In "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No 152, p 283.

(7) Lapporte, S. J.; Toland, W. G. U.S. Patent 3754028, 1973.

(8) However, if it is the reaction of compounds other than the material added or its progeny that limits the formation of product, the absence of an increase in amount of the product upon addiiton of that material is not necessarily citable as evidence against the intermediacy of that material. We did observe in the two experiments, however, the formation of products, not normally formed, tentatively identified as CH_3Cl + CH_3OCH_3 and two-carbon hydrocarbons, respectively. The significance of these observations also is ambiguous since those products may have been consolation fates of the added CH_3OH, i.e., a limiting reagent may not have been available to the CH_3OH in adequate quantity.

(9) The same results were obtained upon addition of HCO_2CH_3 to the $PdCl_2$/65% aqueous HI system. Cf., e.g., Wada, K.; Baba, A.; Wada, N. Japan Patent Application 22745, 1981.

(10) Kaplan, L. U.S. Patent 4224237, 1980.

(11) Some other iodides produced smaller amounts of CH_3CO_2H. ZnF_2, $Zn(CN)_2$, and $Zn(stearate)_2$ were ineffective.

(12) Vauquelin *Ann. Phil.* 1814, *4*, 216.

Table I. Palladium/Acid Induced Reductive Coupling of CO[a]

		product in solution,[b,c] g	
Pd compd	solvent	$HOCH_2CO_2H$[d]	CH_3CO_2H
$PdCl_2$ or Na_2PdCl_4	water	0.1-0.3[e]	
Pd black	water + HCl (2 mmol)	~0.05	
Pd black	water + H_3PO_4 (20 mmol)[f]	~0.05	
$PdCl_2$	30% aq HCl (0.75 h)	0.05	0.03
$PdCl_2$	30% aq HCl		0.10
$PdCl_2$	59% aq H_3PO_4 (0.75 h)	0.08	~0.006

[a] In glass (segregated according to the metal used) for 2 h at 250 °C and 5000 psi of 3/1 CO/H_2, 40 mL of solvent, 10 mmol of palladium, unless noted otherwise. [b] No products of reductive coupling were produced by palladium in the absence of acid; or 30% aqueous HCl, water, or 59% aqueous H_3PO_4 in the absence of palladium; or Pd/NaCl in water; or the otherwise productive $PdCl_2$/ water system in the presence of an equivalent of Bu_3N or py. [c] Typically ~1 g of HCO_2H and a small amount of CH_3OH were produced. [d] When the solvent was 30% aqueous HCl, the product was $ClCH_2CO_2H$; it is reported here as the equivalent weight of $HOCH_2CO_2H$. [e] 0.5-2.0 h. Use of 1 mmol of $PdCl_2$ gave ~0.1 g of $HOCH_2CO_2H$. Reaction at 220 and 280 °C produced smaller amounts of $HOCH_2CO_2H$. Use of 5000 psi of CO and no H_2 gave no products of reductive coupling. [f] Use of 2 mmol of H_3PO_4 gave no products of reductive coupling; the minimum amount of the stronger acid (HCl) necessary for the observation of such products appears to be less than that of the weaker acid (H_3PO_4).

Table II. Palladium/Acid Induced Conversion of CO to Acetic Acid[a]

Pd compd	solvent	CH_3CO_2H produced,[b] g
none	water, 59% aq H_3PO_4, 30% aq HCl, or 48% aq HBr	none
PdI_2	water, 30% aq HCl, 59% aq H_3PO_4,[c] or 32% aq HI	0.01-0.1
none	56 or 65% aq HI	0.02-0.07[d]
$PdCl_2$	65% aq HI (2100 psi)	0.07
$PdCl_2$, PdI_2, or Pd black	56 or 65% aq HI (e)	0.3-0.4[f]
$PdBr_2$	48% aq HBr	0.04

[a] In glass (segregated according to the metal used) for 2 h at 250 °C and 5000 psi of 75/25 CO/H_2, 40 mL of solvent, 10 mmol of palladium, unless noted otherwise. [b] No glycolic acid or methanol was detected. Formic acid was produced, usually in an amount a little greater than that of acetic acid. [c] The ^1H NMR spectrum of the reaction mixture at ambient conditions showed two absorptions in the acetyl region. One grew with time at the expense of the one that had the same chemical shift as observed when acetic acid or lithium acetyl phosphate was added to 59% aqueous H_3PO_4. No products were observed in 85% aqueous H_3PO_4. [d] See ref 1b. [e] 0.5-2.0 h, 75/25-100/0 CO/H_2. The yield was lower when 50/50 CO/H_2 was used. [f] 0.1-0.2 g of propionic acid was produced.[d]

mmol) produced ~0.06 g of CH_3CO_2H in 30% aqueous HCl and ~0.1 g of $HOCH_2CO_2H$ in water; Pt black in 30% aqueous HCl produced neither; $PtCl_2$ in water produced neither in the absence of H_2. Note that the increase in the $CH_3CO_2H/HOCH_2CO_2H$ ratio and in the amount of $HOCH_2CO_2H$ produced as [HCl] increased is similar to the results obtained with palladium (item 7 in the previous paragraph).

The conversion of carbon monoxide to compounds containing $CH_3C(=O)$ and $HOCH_2C(=O)$ groups is now a common reaction.

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Registry No. CO, 630-08-0; $HOCH_2CO_2H$, 79-14-1; CH_3CO_2H, 64-19-7; $PdCl_2$, 7647-10-1; HCl, 7647-01-0; $Rh(CO)_2acac$, 14874-82-9; HI, 10034-85-2; I_2, 7553-56-2; ZnI_2, 10139-47-6; $Ir_4(CO)_{12}$, 18827-81-1; $IrCl_3$, 10025-83-9; Na_3IrCl_6, 15702-05-3; $PtCl_2$, 10025-65-7; Na_2PdCl_4, 13820-53-6; H_3PO_4, 7664-38-2; Pd, 7440-05-3; PdI_2, 7790-38-7; $PdBr_2$, 13444-94-5.

Supplementary Material Available: A general experimental procedure, a unified discussion of "acid catalysis" and "transition metal catalysis," references to the use of ionic hydrogenation catalysts, and a discussion of relevant chemistry of palladium (5 pages). Ordering is given on any current masthead page.

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